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Introduction

The objective of the research is to find means to decrease the rate of optical coloration of ZnO during ultraviolet irradiation in vacuum. This objective will be pursued primarily by supplying recombination centers to intercept the ultraviolet-produced holes and by recombining them with electrons before the holes can do chemical damage. The research is divided into three phases: (1) a study of the hole-electron recombination efficiency* of various adsorbed species on the ZnO surface, (2) a study of the effectiveness of such recombination centers in suppressing chemical changes on the ZnO surface during ultraviolet irradiation in vacuum, and (3) a study of the mechanism through which coloration is induced. In Phase 3, the development of theoretical formulations and apparatus construction, as discussed in earlier reports, was continued.

Recombination Efficiency of Adsorbed Species

The electrolyte measurements, described in the earlier progress reports and the proposal, have been continued to identify candidates for recombination centers and to try to establish some relationship between the chemical nature of the additive species and their efficiency as recombination centers.

An examination of the oxidation of manganese has been started. A reduced form of manganese was produced by controlled reduction of permanganate. The reduced form, Mn(Red) possibly Mn(IV), was found to act as a current doubling agent; that is, as holes were captured, electrons were injected. Thus the oxidation of the Mn(Red) was easily detectable, and the amount was found to correspond qualitatively to the amount

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* Attached is a manuscript, prepared for publication, in which we describe work completed earlier in this investigation.

originally produced. Manganese(VII) is an extremely interesting candidate as a recombination center because of its high electron capture cross section, so the observation of hole capture by the reduced form is encouraging. Quantitative measurement by titration (see previous progress report) of the hole capture cross section has not been performed as yet.

The iodine-iodide couple has been examined to provide further chemical background. A complete list of values of the electron and hole reactivity for the various couples examined so far is presented in Table I. The column Hole Capture Rate is for the lower oxidation state of the elements; the rate is equal to the product of the hole-capture cross section and the sorption constant for the element divided by that for Fe(II). The column Electron Capture Rate is for the higher oxidation state of the element; the rate is equal to the product of electron-capture cross section and the concentration of the sorbed species corresponding to an aqueous solution concentration of 0.01M.

Table I

System	Hole Capture Rate Relative to Fe(II)	Electron Capture Rate 0.01M Solution
Iron	1	8×10^{-8}
Arsenic	0.1	0
Copper	-	5×10^{-9}
Manganese	-	1.6×10^{-4}
Chromium	-	10^{-9}
Sodium Tartarate	-	3×10^{-11}
Iodine	3	10^{-10}

At present, cuprous chloride and cupric chloride are being examined. Also ferric chloride is being examined for the purpose of making a comparison to ferricyanide. We wish to determine the difference in electron capture by the same metallic element in the same oxidation state but with different chemical environment, i.e., ligand. Our conditions for the ferric chloride experiment with single crystal ZnO are similar to the conditions Dr. John Schutt of Goddard Space Center used in preparing an improved TiO_2 coating.

A preliminary examination of the effect of some of these additives is being initiated* by Dr. Schutt. He plans to add ferricyanide and permanganate to a ZnO pigment and try a direct test of the resistance of the pigment to coloration. We are very gratified at the cooperation shown by the NASA scientists in attempting tests even at this early stage of our research. These additives appear to be promising based on our experiments to date but we lack information on application procedures.

Tests of Recombination Efficiency at the ZnO-Vacuum Interface

To test the recombination efficiency of additives, we are using as a first test the inhibition of gas evolution. Thus, we have studied gas evolution from illuminated ZnO in ultrahigh vacuum. The gas evolution, or photolysis, is currently being studied on additive-free crystals. Samples with additives will be studied when the measurements with additive-free crystals are under good control.

Work during this period was concentrated on efforts to: (1) increase the photolysis rate for ZnO free of added recombination centers and (2) establish the chemical composition of the gases evolved from single crystal ZnO during irradiation with photons of different energies. Design and modification of the chamber for constant pressure experiments were completed.

During the previous report period, we showed that irradiation of single crystal samples following a short bakeout (350°C for 4 hours in vacuo) resulted in gas evolution corresponding to a quantum efficiency of 10^{-5} molecules/hole. (The quantum efficiency is measured in terms of molecules of gas evolved per hole reaching the surface.) Since it is planned to use changes in quantum efficiency as a measure of the effectiveness of recombination centers, it is desirable to have as high and as reproducible as possible a value for the quantum efficiency for untreated

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* These plans were formulated as an outgrowth of the JPL-NASA-Lockheed-SRI meeting held at SRI on December 12-13, 1966.

samples, and several techniques of sample preparation were tried to achieve this end.

In one series of measurements, the sample was exposed to 3×10^{-4} torr oxygen at 25°C for one hour. Then the chamber was pumped down to approximately 10^{-8} torr and the sample kept in this environment with some slight intermittent heating of the walls (< 100°C) for several days prior to the u.v. irradiation experiments. Following this treatment, the quantum efficiency increased to 10^{-4} compared with the 10^{-5} in the previous series of experiments. It should be noted that in this series the initial treatment of the sample was a very short dilute nitric acid etch, followed by a thorough water rinse, before introduction into the vacuum chamber and bakeout.

Experiments with lower light intensities were conducted to observe desorption rates at lower time-integrated photon fluxes. These experiments showed approximately the same maximum quantum efficiency with the efficiency value decreasing with increasing total integrated flux. Irradiation of the zinc oxide single crystal from the zinc (0001) face and oxygen ($000\bar{1}$) face gave similar results.

In another set of experiments, the sample was kept dark following bakeout (300°C for 2 hours, $p = 10^{-7}$ torr) to minimize the time-integrated flux incident upon the sample before measurement. No large increase was observed in the efficiency. Some recovery of the efficiency has been observed following standing in the dark for several hours at 10^{-8} to 10^{-9} torr.

Most of the experiments in these series were performed in a chamber operating in a pump-out mode (continuous pumping through a fixed limiting conductance), following establishment of a low stationary base pressure to minimize wall effects that can arise with this mode of operation. Several experiments were conducted at elevated temperatures where sorption of some types of gases by the walls would be diminished. Compared with quantum efficiencies obtained after a regular bakeout only, there were improvements of a factor of four at 230°C and 300°C. These experiments also indicate that the photolysis rate has a low temperature coefficient up to 300°C.

A small magnetic deflection type mass spectrometer (General Electric Model 22 PT103) was incorporated into the gas desorption analysis apparatus to identify the species appearing in the gas phase under ZnO irradiation conditions. The unit has a glass analyzer tube of approximately 400 cc volume and consists of a Nier-type electron bombardment ion source, a 90 degree sector magnetic analyzer section with a 5 cm radius of curvature, and a 10-stage electron multiplier ion detector. The glass analyzer tube was sealed directly to the ZnO irradiation chamber with the ionizer placed 25 cm from the sample although not in direct view of it.

The preliminary data obtained under the pump-out mode indicate that the principal peak appearing during irradiation is mass 32(O_2); minor peaks appeared at mass 17 and 18 (OH and H_2O). Estimates of the partial pressures of the evolved gases indicate that the O_2 pressure reaches 5×10^{-8} torr within 5 minutes, decreasing to about 2×10^{-8} torr after 15 minutes of continuous irradiation, while the water partial pressure increases to about 5×10^{-9} torr during irradiation. No carbon monoxide or nitrogen was observed in these concentration ranges either before or during irradiation of the ZnO example.

As indicated above, sorption by the walls and pumping by the pressure transducers become important factors to consider in the measurement of the sorption or desorption of very small amounts of gases by a sample. To minimize these effects, we plan to conduct the experiment at constant pressure, using a controlled oxygen leak operated by a feedback mechanism. Under these conditions, the amount of gas sorbed or desorbed is measured by changes in the feed rate from the oxygen leak required to maintain steady state conditions.

We have incorporated such a design into our irradiation chamber apparatus. The apparatus consists of an oxygen reservoir connected to a servo-driven valve. Between the low pressure side of the servo valve and a calibrated conductance is located the upstream ionization gauge. The low pressure side of the calibrated conductance is connected to the irradiation chamber that contains the sample, a downstream ionization gauge, and the mass spectometer. The irradiation chamber is connected to

the pumps (ion and sublimation) through a known second conductance. The calibrated conductance between an oxygen resevoir and the irradiation chamber acts as a flow monitoring device; the flow rate into the chamber is determined from the pressure difference across this conductance measured by the two ionization gauges. The operation of the servo valve is controlled by a signal from the chamber ionization gauge for the purpose of keeping pressure in the chamber constant.

Experiments are being started in which measurements of the desorption rates of various gases from ZnO are made under conditions of constant oxygen partial pressures of 10^{-9} to 10^{-8} torr.

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MECHANISM OF CATHODIC PROCESSES ON THE SEMICONDUCTOR ZINC OXIDE*

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ABSTRACT

The cathodic reduction of the aqueous ferricyanide ion was investigated on a single crystal zinc oxide electrode. The experimental results substantiate that this chemical reduction process obeys the model used in semiconductor physics for electron capture by surface states. It is concluded that the rate determining step of the reduction process is the capture of electrons from the conduction band of the ZnO by the sorbed ferricyanide ions. This process was shown to be irreversible, i.e., electrons are not transferred from sorbed ferrocyanide (reduced ferricyanide) to the semiconductor electrode. The capacitance, voltage and current were measured as a function of the concentration. The rate of ferricyanide reduction was measured by the current and was found to be first order in sorbed ferricyanide ion and first order in the electron concentration at the surface. The electron concentration at the surface of the electrode was determined from the capacitance-voltage measurement.

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* Part of this work was supported by a group of industrial companies sponsoring a program in heterogeneous catalysis and part of this work was performed for Jet Propulsion Laboratory, California Institute of Technology, sponsored by National Aeronautic and Space Administration under Contract NAS7-100.

The sorption isotherm for ferricyanide was found to be linear in concentration over the range from 7×10^{-5} to 0.7 Molar.

INTRODUCTION

The understanding of the role of the solid in charge transfer process on the surface is an important objective in electrochemistry and heterogeneous catalysis. With this objective, we have measured the current-voltage characteristics of the cathodic reduction of aqueous ferricyanide ion using a single crystal of the n-type semiconductor, zinc oxide. Primarily by measuring the voltage-capacity characteristics, we have concluded that the rate of the cathodic process (the measured current) is determined by charge transfer from the solid to the sorbed species. Evidence will be presented that the charge transfer process is an irreversible bimolecular reaction governed by the concentration of the conduction-band electrons at the surface and the concentration of sorbed oxidizing agent. Thus, the role of the solid is two fold: to provide electrons at the surface and to form electronic surface states with the sorbed oxidizing agent.

While Dewald has reported[1] in detail data for the voltage-capacitance behavior of the ZnO/electrolyte system in the absence of reducing or oxidizing agents, his reported[2] data for the current-voltage behavior with hexacyanoferrate ions was very incomplete. This lack of experimental data for voltage, capacitance, current, and concentration relations prompted us to investigate in detail this chemically simple ferrous-ferric redox couple on a single face of single crystal zinc oxide. We believed this to be important because our previous studies,[3] carried out in connection

with the ZnO photocatalyzed reaction of oxygen and formate ions indicated that electrode processes on Zno can be irreversible. Our conclusion concerning reversibility was in disagreement with Dewald's interpretation for $Fe(CN_6^{-3})$, which was in terms of a reversible redox reaction characterized by a Helmholtz potential. In a review paper[4] Gerisher came to the same conclusion as Dewald. In this communication, we will present detailed evidence for the irreversibility of cathodic processes on ZnO as illustrated by the reduction of $Fe(CN)_6^{-3}$.

EXPERIMENTAL

The borosilicate glass electrochemical cell used contained a zinc oxide single crystal as one electrode, a platinum wire as the working electrode, and a saturated KCl calomel reference electrode. The (0001) face of the crystal was used after lapping and then etching with 85 percent H_3PO_4 for a minimum of ten minutes. The area of zinc oxide exposed to the electrolyte was the order of $6mm^2$.

The electrolyte contained 1M KCl and was buffered with BO_2^-/HBO_2 (0.2M in total boron) to a pH of 8.8 ± 0.1. The ferri- and ferrocyanide were added as the potassium salts and the pH of the buffer was adjusted if necessary. The chemicals employed were Reagent grade and were used without purification. All electrical measurements were made with solutions deoxygenated in situ by bubbling with unpurified tank nitrogen. In no case could more than 5 percent of the current be attributed to any substance other than $Fe(CN)_6^{-3}$. That is, the current at any given voltage was increased by at least a factor of 20 with the addition of $Fe(CN)_6^{-3}$ to the KCl buffered solution.

Three types of measurements were made: (1) the current through the ZnO, (2) the capacitance between the ZnO and the platinum electrodes, and (3) the voltage of the ZnO with respect to a saturated KCl calomel electrode (SCE). The values of the capacitance, voltage, and current reported are steady state measurements and were shown to be independent of stirring. All measurements were made in the dark. The capacitance was measured at a frequency of 1 kc.

Two types of measurements, the current as function of the applied voltage and the capacitance as a function of voltage, were made at various ferricyanide concentrations from 0.7M to 7×10^{-5}M with and without added ferrocyanide. Figures 1 and 2 show typical results for the two types of measurements.

Figure 1 shows data for the cathodic current, J, vs the applied voltage, V, for two solutions both containing 7×10^{-3} ferricyanide. The solutions differ only in that one contains no ferrocyanide and the other was 7×10^{-2}M in ferrocyanide. The data for both solutions are identical within experimental error. The linearity of the dependence of log J vs V shown in Figure 1 is typical for all solutions examined. In the range of current investigated, from 1 to 100 na, plots of the log J vs V for all solutions showed slopes corresponding to 60 $\pm$ 5 mv per decade change in cathodic current. Typically all solutions including those containing ferrocyanide gave anodic currents below 5 na up to anodic voltages as high as 10 V vs SCE.

Figure 2 shows the voltage dependence of the capacitance plotted as $1/C^2$ vs V. The linearity of the experimantal data is typical of all

solutions investigated including those free of iron salts. The value of the ZnO voltage vs SCE at $1/C^2 = 0$ is called the flat band voltage, V_0. In practice, the linear portion of $1/C^2$ vs V is extrapolated to $1/C^2 = 0$, since deviations from simple theory are known[1] to occur near V_0. The surface barrier, V_S, is related to the ZnO voltage vs SCE, V, by Eq. 1; in our experiments V_S always has a positive value.

$$V_S = V - V_0 \qquad (1)$$

The significance of the parameters, the surface barrier and the flat band voltage will be presented in the "Discussion" in terms of semiconductor concepts. For the present, they will be taken simply as convenient variables.

The values of V_0 for the various solutions reported in this paper ranged from -0.370 to -0.410 V vs SCE. The variations in V_0 were not systematic and hence their origin is not known.

Figure 3 is plot of the log of the $[Fe(CN)_6^{-3}]$ vs the surface barrier, V_S, at constant current of 10 na. The plot is linear and the slope corresponds to a surface barrier change of 0.06 V per tenfold change in concentration.

The above experimental data can be summarized empirically by Eq. (2), where k is a proportionality constant independent of voltage and concentration.

$$J = k\,[Fe(CN)_6^{-3}]\,\exp\left\{(V_0 - V)/0.025\right\} \qquad (2)$$

Preliminary investigations with several other oxidizing agents, including Cu(II), I(0), Mn(VII), O(-I), indicate similar behavior, at least qualitatively.

THEORETICAL MODEL

We will present arguments supported by the above results to show: (1) the changes in the applied voltage all occur within the semiconductor and that the cathodic current is dominated in its voltage dependence by the properties of the semiconductor; (2) the electrochemical reduction reaction is a one-electron process and is irreversible since the reverse reaction, the oxidation of Fe(II), does not proceed at an appreciable rate. The lack of the oxidation reaction is attributed to the difficulty of injecting electrons from sorbed oxidizing agent into the conduction band of the ZnO; (3) the reaction rate is first order in the concentration of reducible species on the surface.

The arguments are most easily presented in terms of an electronic energy band diagram. Figure 4 shows a band diagram of the n-type semiconductor ZnO with acceptor surface states. The abscissa is distance from the zinc oxide surface which is in contact with the electrolyte solution; the ordinate is the potential energy of an electron. Within the solid there are three energy regions: two have allowed electronic levels, the valence and conduction bands; separating them is a forbidden region, the energy gap which is about 3 eV. Within the gap, there is a donor level located slightly below the bottom of the conduction band. The donors associated with this level result from the stoichiometric excess of zinc in zinc oxide and are presumably either interstitial zinc atoms or oxide ion vacancies. Since they are ionized at room temperatures, they are shown as "+." The conduction band electrons are indicated by "-" at the bottom of the conduction band. It should be noted that the

ionized donors are immobile charges at room temperature in contrast to conduction band electrons.

An allowed electronic energy level on the surface is indicated by X; such a surface state can be created by sorption of a chemical species from the electrolyte solution. It is shown at an energy, E, below the top of the conduction band. We will restrict this symbol to the surface state created by sorption of $Fe(CN)_6^{-3}$. When this state is electronically occupied (X^-) by the addition of an electron it is equivalent to sorbed $Fe(CN)_6^{-4}$.

A potential gradient, in the region $0 < x < x_0$, is indicated by the bending of bands. The extent of the bending is indicated by the energy of the surface barrier, qV_s, where q is the electronic charge. The surface barrier is associated with the double layer formed by the ionized donors in the electron depletion layer ($0 < x < x_0$) and the compensating negative charge arising from charged surface states and ions in the electrolyte. Because of the electrical compensation of the ionized donors in the electron depletion region by ions in solution, the surface barrier can be controlled by the externally applied voltage in the electrochemical cell. It should be noted that in the interior of the crystal ($x > x_0$) the charge of ionized donors are compensated by the negatively charged conduction band electrons.

The surface barrier can be measured experimentally by the capacitance. A rigorous development of the interpretation of the experimentally measured capacitance and voltage is given in the appendix. The surface barrier, V_s, is related to the depth of the depletion region x_0 (shown in Fig. 4)

by the Schottky relation,[5] Eq. (3), where q is the electronic charge, N_D the density of the ionized donors, ϵ the dielectric constant for zinc oxide, and ϵ_0 the permittivity of vacuum.

$$V_S = qN_D x_0^2 / 2\epsilon\epsilon_0 \tag{3}$$

The value of V_S can be obtained experimentally when the Schottky relation is valid through the capacitance measurement. The differential capacitance, C, can be used to determine the thickness of the depletion layer by the parallel plate capacitor relationship, Eq. (4), where A is the area.

$$x_0 = \frac{A\epsilon\epsilon_0}{C} \tag{4}$$

Substitution of Eq. (4) in Eq. (3) gives Eq. (5), a relationship between the surface barrier and a measurable quantity, the capacitance.

$$V_S = \tfrac{1}{2}\, qN_D A^2 \epsilon\epsilon_0 (1/C^2) \tag{5}$$

Since we found experimentally for each solution that V is linearly dependent on $1/C^2$ (e.g., Fig. 1) and from the above semiconductor theory V_S has the same dependence on $1/C^2$, it follows that V_S differs from V by a constant given in Eq. (1). This constant, V_0, is the sum of: the voltage difference between the Fermi levels at the surface and in the interior of the crystal at flat band condition, the Helmholtz and Gouy potentials at the solution side of the ZnO electrode and the calomel electrode, and any possible voltage drop between the ZnO and its metallic contact. Following Dewald,[1] we adopt the simplest explanation for the linearity of $1/C^2$ with V for a given solution and crystal. The explanation is that the component voltages of V_0, including the Helmholtz potential at

the ZnO/electrolyte interface, remain invariant as a function of V. It should be noted that the Helmholtz voltage must be presumed to be independent of the hexacyanoferrate species, either in the oxidizing or reducing form, since we found that V_0 was essentially constant for all solutions at pH = 8.8.

This agreement of theory and experiment shows that variations in applied potential appear only as variations of potential within the electrode and that the potentials on solution side of the electrode, i.e., Helmholtz (and Gouy) are invariant. With the demonstration that the voltage variation is in the surface barrier, we will procede to show that electron transfer is the rate-limiting step in the reduction reaction.

The model to which we shall compare our results involves two parts. First, the electron transfer process is governed by semiconductor theory for irreversible electron capture by unoccupied surface states. Second, the formation of surface states is governed by a linear isotherm for sorption from solution.

The electron current density, J, passing from the conduction band of a semiconductor to a single type of surface state for an irreversible reaction should have the magnitude given[5] by Eq. (6).

$$J = q\,\bar{c}\,\sigma\,[X]\,n \qquad (6)$$

The current is proportional to the average thermal velocity of electrons, $\bar{c}$; the concentration of the unfilled surface states, [X]; the cross section of this state for electron capture, σ; and the electron density at the surface, n. The electron concentration in the conduction band at the surface, n, is given[6] by the ionized donor density of the ZnO multiplied

by the Boltzmann factor associated with V_s, i.e., $N_D \exp(-qV_s/kT)$; therefore, Eq. (6) can be expressed as Eq. (7).

$$J = q \bar{c} \sigma [X] N_D \exp(-qV_s/kT) \quad (7)$$

Therefore, Eq. (7) contains the assumptions that the conduction band electrons at the surface are in thermal equilibrium with the interior and that their concentration at the surface is not appreciably disturbed by the cathodic currents. Implicit in this formulation is the absence of any tunneling effects; we believe these should be negligible.

The theoretical relationship, Eq. (7), between the current and the surface barrier can be compared to our experimental finding, Eq. (2), in order to find the relationship between the [X], the density of unfilled surface states and the $[Fe(CN)_6^{-3}]$, the concentration of oxidizing agent in solution. Since (q/kT) at room temperature has a value of 1/0.025 a comparison of Eq. (7) and Eq. (2) gives Eq. (8).

$$k [Fe(CN)_6^{-3}] = q \bar{c} \sigma [X] N_D \quad (8)$$

The simplest explanation for the linearity of the concentration of sorbed ferricyanide with the concentration in solution is to assume the linear isotherm expressed by Eq. (9) with the equilibrium constant K.

$$K = [X]/[Fe(CN)_6^{-3}] \quad (9)$$

This assumption implies that the rate of the electron capture process is slow compared to the rate of desorption of $Fe(CN)_6^{-3}$ so that the [X] is not appreciably lowered by the current of the cathodic reaction. This simple assumption was borne out experimentally in the ranges of current and concentrations investigated since the current, J, was linearly

proportional to the concentration in solution, $[Fe(CN)_6^{-3}]$ at constant V_s. Equation (7), the current as a function of the density of unfilled surface states, may be written in terms of the experimental variable, the concentration ferricyanide ion in solution, by the use of Eq. (9) to give Eq. (10).

$$J = q\,\bar{c}\,\sigma\,K\,[Fe(CN)_6^{-3}]\,N_D \exp(-qV_s/kT) \qquad (10)$$

The substantial agreement of the theoretical model with the experimental results (the 0.06V change in the surface barrier per decade change in iron concentration and the linear proportionality between the current and the iron concentration) leads to the following conclusions:

1. The rate limiting step in this reduction process is the transfer of electrons from the solid to the surface state. The rate is first order in the density of electrons at the surface of the solid, $N_D \exp(-qV_s/kT)$, and first order in the density of unfilled surface states, $[X]$.

2. In the current and concentration ranges investigated the density of unfilled states is determined by the equilibrium linear adsorption isotherm for $Fe(CN)_6^{-3}$; moreover the desorption of filled surface states as $Fe(CN)_6^{-4}$ is rapid compared to the electronic process.

3. The unidirectional nature of the electron transfer assumed in our model is confirmed by the lack of dependence of the current on the $Fe(CN)_6^{-4}$ concentration.

DISCUSSION

Before analyzing in detail the implications of the semiconductor surface state model and our results, it may be helpful to describe some reasons accounting for observing the simple behavior of surface states in the zinc oxide/ferricyanide system. The first reason is connected with the electrode material being a semiconductor and the second is connected with the chemical simplicity of the behavior of the hexacyanoferrate ion.

For a semiconductor, in contrast to a metal, it is possible to vary the electron concentration at the surface by the applied voltage and to measure this concentration by the capacitance. However, starting with the classical semiconductor/electrolyte investigations of Brattain and Garrett[7] it has become evident that not all semiconductor/electrolyte systems are simple, e.g., Ge.[8] We feel that the simplicity of our results add to the many advantages that Body[9] has recently pointed out for ZnO. Dewald's[1] pioneering work with ZnO/electrolyte showed that this system obeyed simple solid-state theory for a semiconductor. In the course of preliminary studies we did not find any common laboratory reducing agents which would inject electrons into ZnO.

The second reason for predicting a simple behavior of the $ZnO/Fe(CN)_6^{-3}$ system is concerned with the chemical nature of the six coordinate iron. Ferricyanide ion on sorption would be expected to form a single type of surface state and the chemical reduction of this surface state would be expected to be simple electron capture without any chemical rearrangements. Our expectation was based on the known aqueous chemistry of

hexacyanoferrate ions, i.e., one-equivalent reduction of Fe(III) normally occurring by single electron transfer without atom transfer (both oxidation states are relatively inert to chemical substitution).

It should not be anticipated that all solutions containing oxidizing agents will exhibit the simple behavior described by Eq. (10). First, a multiplicity of types of unfilled states may be present; these could arise from factors such as multi-equivalance of the oxidizing agent, inhomogenous surfaces, and the presence of more than one oxidizing agent in the solution. For such cases Eq. (6) must be replaced with Eq. (11) where the summation is carried out over the concentration of the various surface states, X_i, with the appropriate electron capture cross-sections, σ_i.

$$J = q\, n\, \bar{c} \sum_i \sigma_i [X_i] \qquad (11)$$

While Eq. (11), involving surface concentrations, is always valid for irreversible electron capture processes, a second class of complication can arise. This class arises when the current is expressed as a function of solution concentrations of the oxidizing agents and may involve factors such as: multi-equivalence of the oxidizing agents, slow sorption or desorption, or non-linearity of isotherms. For such kinetic features, the current can become non-linear in electron concentration at the surface as well as solution concentrations.

It has normally been the custom to treat theoretically semiconductor electrodes by an approach equivalent to metal electrodes and to discuss reduction or oxidation electrochemistry in terms of deviation from the reversible potential. This approach is theoretically valid, but the

model may be of little value in interpreting experimental results. The invariance of the Helmholtz potential and the irreversibility of the current are two indications that the reversible potential model is not applicable here.

First we will discuss the invariance of the Helmholtz voltage for the $ZnO/Fe(CN)_6^{-3}$ system as a function of concentration and measured current. Such behavior contrasts with a metal electrode in which the net current is normally controlled through deviations from the reversible redox potential. Basically the reason such a situation can arise is that the current due to the reduction of $Fe(CN)_6^{-3}$ is only a small fraction of the reversible currents passing through the Helmholtz layer, and these reversible currents determine the Helmholtz voltage. By the argument presented by Dewald,[1] changes in Helmholz potential at the ZnO electrode should be manifested by changes in the values of the flat band voltage, V_o. Conversely, changes in the flat band voltage with changes in the chemical composition of the solution, in principle, can be attributed to variations in the Helmholtz and/or surface voltage of the ZnO electrode.

Experimentally, we found only small random variations in the flat band voltage as a function of $Fe(CN)_6^{-3}$ concentration and the ratio of the concentrations of $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$. Since it seems unlikely that changes in the surface voltage (determined by the Fermi level at the surface vs the interior when the bands are flat) should exactly compensate changes in the Helmholtz voltage, we conclude that both the Helmholtz and surface voltage at the flat band condition are independent

of the concentrations of hexacyanoferrate species. Experimentally for any single solution composition, the value of V_0 remains constant as a function of the applied voltage as observed by the straight line behavior typified by Fig. 2. From this observation, we conclude that the Helmholtz voltage is independent of the dominant reduction process on the ZnO, the reduction of ferricyanide. In preliminary experiments, we have found that the flat band voltage is sensitive to the pH of the solution but insensitive to the several reducing and oxidizing agents investigated.

It is therefore our belief that the Helmholtz voltage of the electrode is not associated with any electron transfer redox reaction occurring on the surface, but should be ascribed to proton transfer, or to some equivalent chemical process which does not involve electrons or holes.

Next we shall consider the currents passing between the surface and the interior of the semiconductor. In our semiconductor surface state model, as previously discussed, the flow of negative current from the interior to the surface is associated with an activation energy of qV_s which arises from the endothermicity of moving an electron in the conduction band from the interior to the surface. The reverse process is the oxidation and could occur by transfer of an electron from the reduced sorbed species to the bottom of the conduction band in the interior of the semiconductor. The latter process would be expected to have an activation energy equal to E, the energy difference between the surface state and the bottom of the conduction band at the surface (Fig. 4). For the surface state on ZnO due to the hexacyanoferrate, the value of E could be as high as 3 eV. If the value of E is high, the rate of the oxidation process can be extremely low.

Thus deviations from a "reversible potential" on the solution side (Helmholtz) or within the semiconductor can not be used to describe the net current flowing through the electrochemical cell. Furthermore, the experimental condition of zero net current does not correspond to some "reversible potential" analogous to a metal electrode since the rate of the anodic process in the semiconductor model is always essentially zero.

Experimentally, however, we do observe small residual net anodic currents. The residual anodic current observed with ZnO can sometimes be attributed to stray ultraviolet illumination (energies greater than the band gap), which produces holes. In other cases, thermal generation of hole-electron pairs in the bulk will provide a higher anodic current than electron injection having an activation energy E. In either case, the potential at zero current is not the reversible potential of a chemical redox reaction but is the result of opposing currents, both of which are determined by physical processes not occurring in the solution.

We believe the major sources of the low anodic currents in the dark may be imperfections and impurities on the surface of the sample. The results with our crystals are consistant with this notion, i.e., the saturation dark anodic current varied randomly from 0.1 to 10 na/cm^2 with repeated etchings in phosphoric acid under presumably identical conditions. On the other hand, the addition to the solution of the reducing agent, $Fe(CN)_6^{-4}$, had a negligible effect on the anodic current.

This behavior is probably quite typical of electrochemical reactions on wide band gap semiconductors and theoretical analysis based on reversible reactions may often be very misleading.

The last point of our discussion concerns the surface state capacitance, C_{ss}, which is defined[5] as dQ_{ss}/dV where Q_{ss} is the charge in the surface states. We will present arguments to show that there is no inconsistancy between our experimental results which indicate the absence of a surface state capacitance and our theoretical model which depends on the existance of surface states. It should be emphasized that the experimental absence of a surface state capacitance in a semiconductor/electrolyte system should not be taken to imply the absence of surface states. This point is important because the absence of a surface state capacitance has often[1,5] been taken to indicate the absence of surface states.

Experimentally, the absence of a surface state capacitance in parallel with the space charge is shown by the linearity of $(C)^{-2}$ with V. The reasoning is based on the expectation that, in general, $(C_{ss})^{-2}$ will not be linear with V. The details of the formulation of the various capacitances and voltages in a semiconductor/electrolyte system are contained in the appendix. It should be recalled that all the solutions studied in our investigation showed a linear relationship between $(C)^{-2}$ and V.

There are two possible reasons why a capacity C_{ss} is not observed: one, the implicit assumptions of the derivation are not met; and second, there are no surface states over the region spanned by the surface Fermi level as V is varied. We will present arguments that both of these causes are present with most semiconductor/electrolyte systems.

Implicit in the derivation of the surface state capacity is the assumption that the charge dQ_{ss} is stored from the semiconductor side and

is returned to the semiconductor when the voltage increment dV is removed. This assumption is not met for two types of surface states: those that are electronically irreversible (i.e., charge cannot transfer in both directions) and those that are reversibly adsorbed from solution. If the states are irreversibly charged within the period of the a.c. signal, then the charge will not be returned to the semiconductor and the states will not act as charge storage centers. If the states are desorbable, so that they maintain equilibrium with the solution, they will simply lower the real part of the impedance rather than the capacitative part.

The second reason for the inability to observe a capacitance for surface states is connected with a pinned surface Fermi level. A pinned surface level, i.e., constant qV_f in Fig. 5, can arise from the presence of second surface state which cannot store charge from the semiconductor. This second surface state may be of two types: (a) present at a high density on the surface, either formed by irreversible or reversible sorption, or (b) present at low density and formed by reversible sorption. The effectiveness of type (a) in pinning the Fermi level is self evident. Type (b) is effective since any attempt at changing the surface Fermi level by changing the applied voltage is prevented by sorption or desorption of type (b) surface states in the appropriate state of oxidation. Thus, the existance of a low density of sorbable-desorbable surface states can prevent observance of a capacitance for another surface state that meets the normal requirements for observation.

In summary, in order to observe a surface state capacitance the surface states must be: (1) electronically reversible within the period

of the a.c. signal; (2) nondesorbable from the semiconductor; and (3) in contact with an electrolyte free of chemicals that can rapidly exchange charge with the surface state or with the semiconductor in order to prevent pinning the surface Fermi level.

In the case of our ZnO studies, none of these criteria were met, according to the evidence. There have been no reversible surface states identified in our studies, most of the chemical species examined were appreciably soluble in both the oxidized and reduced forms and species normally were available that could be adsorbed and could pin the Fermi level. However, it is possible that common contaminants present in our solutions were sufficient to pin the Fermi level.

SUMMARY

We have shown, by analysis of the one-equivalent reduction of the ferric iron, that for semiconductors the electronic activation energy can dominate the rate of electrochemical reactions and a simple surface state trapping law describes the process. We have also shown that the reaction is irreversible and an unknown oxidation reaction (not oxidation of ferrous) is important in defining the "zero current" potential. In addition, we found that adsorption of ferricyanide ion on zinc oxide follows a linear isotherm.

N67-18551

Appendix

ANALYSIS OF SEMICONDUCTOR - ELECTROLYTE CAPACITY

In order to be clear regarding the origin of the capacity measured, and to distinguish space charge capacity, surface state capacity, and other possible contributions to the measured capacity, it is appropriate to examine in detail the distribution of voltage and stored charge for the electrolyte-semiconductor interface. To maintain some measure of simplicity, we will assume that the impedance at the working electrode and elsewhere in the circuit is negligible compared to the impedance at the semiconductor-electrolyte interface, so that changes in voltage occur in the latter region.

The applied voltage with respect to the electrolyte will be given by $-V_e$, where V_e is the potential of a negative charge* in the solution with respect to the bulk Fermi potential.

$$V_e = V_s - V_f + V_H + V_c = V + \text{const} \qquad (12)$$

where qV_s is the height of the surface barrier, qV_f is the energy difference between the Fermi energy at the surface and the conduction band at the surface, and eV_H is the energy difference through the Helmholtz solution (and Gouy) double layer. The constant V_c represents the potential difference between the conduction band and the Fermi potential in the bulk semiconductor. The measured voltage with respect to SCE, V,

* This potential of a negative charge is used to allow ready comparison with the normal band diagram.

differs from V_e by a constant representing terms such as the Helmholtz potential drop at the calomel.

Figure 5 shows the corresponding band diagram for the energy of an electron, showing E_{FB} and E_{FS} as the Fermi energy in the bulk semiconductor and on the surface respectively, and V_H as the difference between the solution potential, V, and the surface potential, E_{FS}/q, for the electron.

A change in applied voltage, dV, is given by Eq. (13).

$$dV = dV_s + dV_H - dV_f \tag{13}$$

Storage of charge on the semiconductor can occur in surface states or in the space charge region.

$$dQ = dQ_{ss} + dQ_{sc} \tag{14}$$

On the electrolyte side, we assume charge storage is all on the electrolyte side of the Helmholtz double layer.

There will be a relationship between the change of surface barrier and the charge stored in the space charge region. In the case of a depletion layer at the surface, this becomes the Shottky relation, equivalent to Eq. (3) in the text, but we will leave it in the general form[5] of Eq. (15).

$$dQ_{sc}/dV_s = f(Q_{sc}) \tag{15}$$

The measured capacity, $C_m = dQ/dV$, is given, from (14), by

$$\frac{dQ}{dV} = C_m = dQ_{ss}/dV + (dQ_{sc}/dV_s)(dV_s/dV)$$

$$= dQ_{ss}/dV + f(Q_{sc})\left\{1 + dV_f/dV - dV_H/dV\right\} \tag{16}$$

We will define the surface state capacity[5] C_{ss} as

$$C_{ss} = dQ_{ss}/dV = (\partial Q_{ss}/\partial V_s)(dV_s/dV) + (\partial Q_{ss}/\partial V_f)(dV_f/dV) + (\partial Q_{ss}/\partial V_H)(dV_H/dV) \quad (17)$$

It should be noted that Dewald[1] defined C_{ss} as $\partial Q_{ss}/\partial V_s$ which is identical to the above definition when the changes in the applied voltage occur only within the depletion region.

Now the change in Helmholtz potential V_H will depend on the charge dQ, which has been stored on the effective Helmholtz capacity, where

$$1/C_H = \partial V_H/\partial Q \quad (18)$$

plus changes in the Helmholtz double layer arising from changes in the "chemical" behavior of the solid when V_f or V_s is changed. This change in Helmholtz potential is expressed in Eq. (19).

$$dV_H/dV = (\partial V_H/\partial Q)(dQ/dV) + (\partial V_H/\partial V_f)(dV_f/dV) + (\partial V_H/\partial V_s)(dV_s/dV)$$
$$= (1/C_H)(dQ/dV) + g(V_H, V_f, V_s) - dV_f/dV \quad (19)$$

where

$$g \equiv (dV_f/dV)(1 + \partial V_H/\partial V_f) + (dV_s/dV)(dV_H/\partial V_s) \quad (20)$$

We will assume for simplicity that C_H is similar to the Helmholtz capacity at a metal/electrolyte interface, and at a later stage in the derivation we will assume $C_H \gg C_m$ and it will be neglected. The function g depends on the electrochemical properties of the interface and cannot be defined further without detailed physical knowledge of the electrochemical processes.

Then the measured capacity becomes

$$C_m = C_{ss} + C_{sc}(1 - g - C_m/C_H) \quad (21)$$

where we have defined $C_{sc} \equiv f(Q_{sc})$. (22)

Then

$$1/C_m = 1/\left\{C_{ss} + C_{sc}(1-g)\right\} + 1/\left\{C_H\,(1-g + C_{ss}/C_{sc})\right\} \qquad (23)$$

The two terms thus represent two capacitors in series, one dominated by the Helmholtz capacity, and the other determined primarily by the surface state and the space charge capacities.

If we assume $C_H \gg C_m$, i.e., the Helmholtz capacity observed with metal electrodes is much greater than the capacity measured, then the last term may be neglected. This is confirmed further if a linear V vs $1/C_m^2$ relation is normally observed, for the last term contains no factors leading to this relationship. Then (23) is approximated by(24)

$$C_m = C_{ss} + C_{sc}\,(1-g) \qquad (24)$$

When C_{ss} of Eq. (24) is negligible, as found for ZnO, the equation becomes

$$C_m = C_{sc}\,(1-g) \qquad (25)$$

A linear relation between V and $1/C^2$ is indicative that g is either constant, independent of V, or is zero. Moreover, for ZnO, Dewald[1] found that any finite g must be independent of the donor density and in the present work we have found the slope independent of the concentration of reducible or oxidizable species in solution.

From Eq. (20), this requires that, if V_f is a function of V the derivative is very low or constant, independent of donor density and surface state density. The most likely interpretation is that dV_f/dV is low, i.e., the surface Fermi level does not change appreciably with applied

voltage. Similarly, the value of $\partial V_H/\partial V_s$ is most likely very low rather than constant; otherwise, the donor density change and surface state change would be expected to change its value. This is consistent with the earlier interpretation that the Helmholtz potential is associated with a process other than the reduction process studied.

It appears that, for our system, we can justify the approximation that

$$C_m = C_{sc} \tag{26}$$

Because of the action of reversibly adsorbed species in pinning the surface Fermi level, as discussed in the text, it may be reasonable to assume Eq. (26) for most semiconductor/electrolyte systems with $C_m \ll C_H$, as long as the current drawn from the system is low enough that adsorption equilibrium is maintained. However, the validity of Eq. (26) should not be construed as indicating the absence of surface states.

REFERENCES

1. J. F. Dewald, J. Phys. Chem. Solids 14, 155 (1960); Bell Systems Tech. J. 39, 615 (1960).

2. J. F. Dewald in Surface Chemistry of Metals and Semiconductors, Ed. John Wiley, New York, 1960.

3. S. Roy Morrison and T. Freund, submitted for publication.

4. H. Gerisher in Surface Chemistry of Metals and Semiconductors, Ed. H. C. Gatos, John Wiley, New York, 1960.

5. A. Many, Y. Goldstein, and N. B. Grover, Semiconductor Surfaces, John Wiley, 1965.

6. W. H. Brattan and Barteen, Bell Systems Tech. J. 32, 1 (1953).

7. W. H. Brattan and C. G. B. Garrett, Bell Systems Tech. J. 34, 129 (1955).

8. H. Gerischer, Ann. Rev. Phys. Chem. 12, 227 (1961).

9. P. J. Body, J. Electroanalytical Chem. 10, 199 (1965).

FIGURES

Figure 1 Current Dependence on Voltage at pH = 8.8 and $7x10^{-3}M$ $Fe(CN)_6^{-3}$: ●, no added $Fe(CN)_6^{-4}$; O, $7x10^{-2}M$ $Fe(CN)_6^{-4}$ added.

Figure 2 Voltage Dependence of Capacitance for $7x10^{-4}M$ $Fe(CN)_6^{-3}$

Figure 3 Surface Barrier as a Function of Concentration at 10 na Current

Figure 4 Energy Band Diagram

Figure 5 Potential Energy Diagram for Electrons

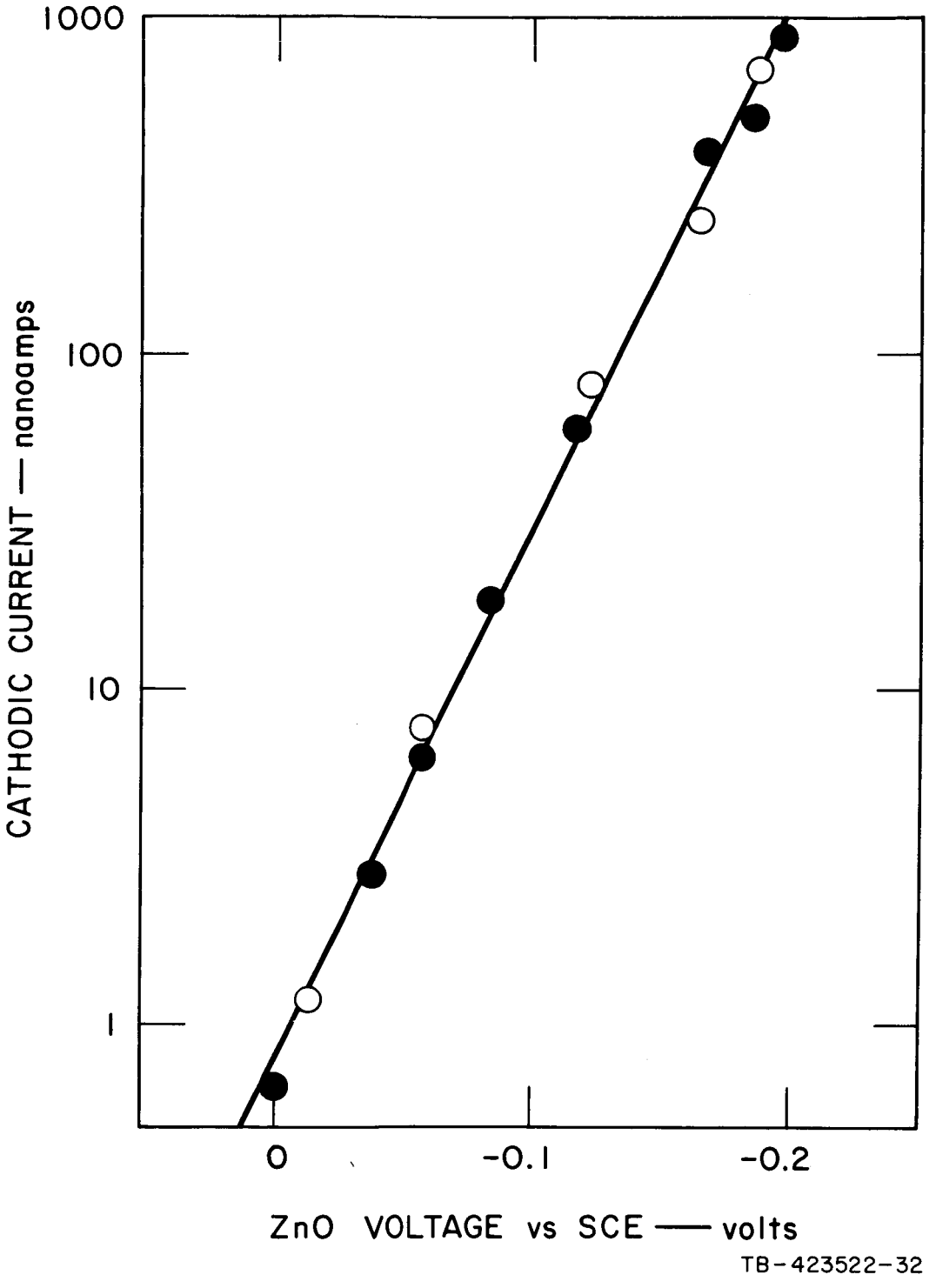
1000
100
10
1
CATHODIC CURRENT — nanoamps
0
-0.1
-0.2
ZnO VOLTAGE vs SCE — volts
TB-423522-32

FIG. 1

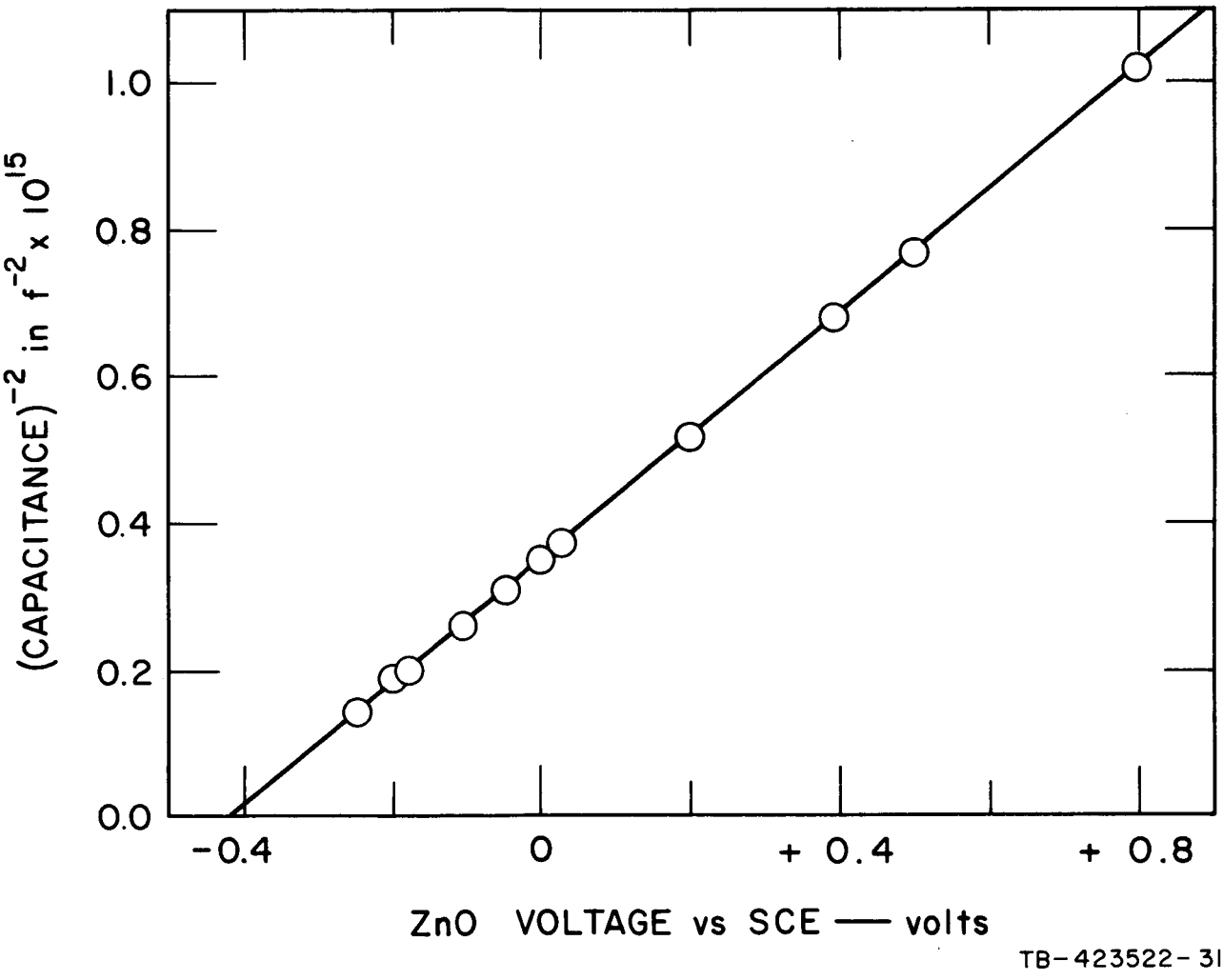
1.0
0.8
0.6
0.4
0.2
0.0
(CAPACITANCE)$^{-2}$ in $f^{-2} \times 10^{15}$
-0.4
0
+ 0.4
+ 0.8
ZnO VOLTAGE vs SCE — volts
TB-423522-31

FIG. 2

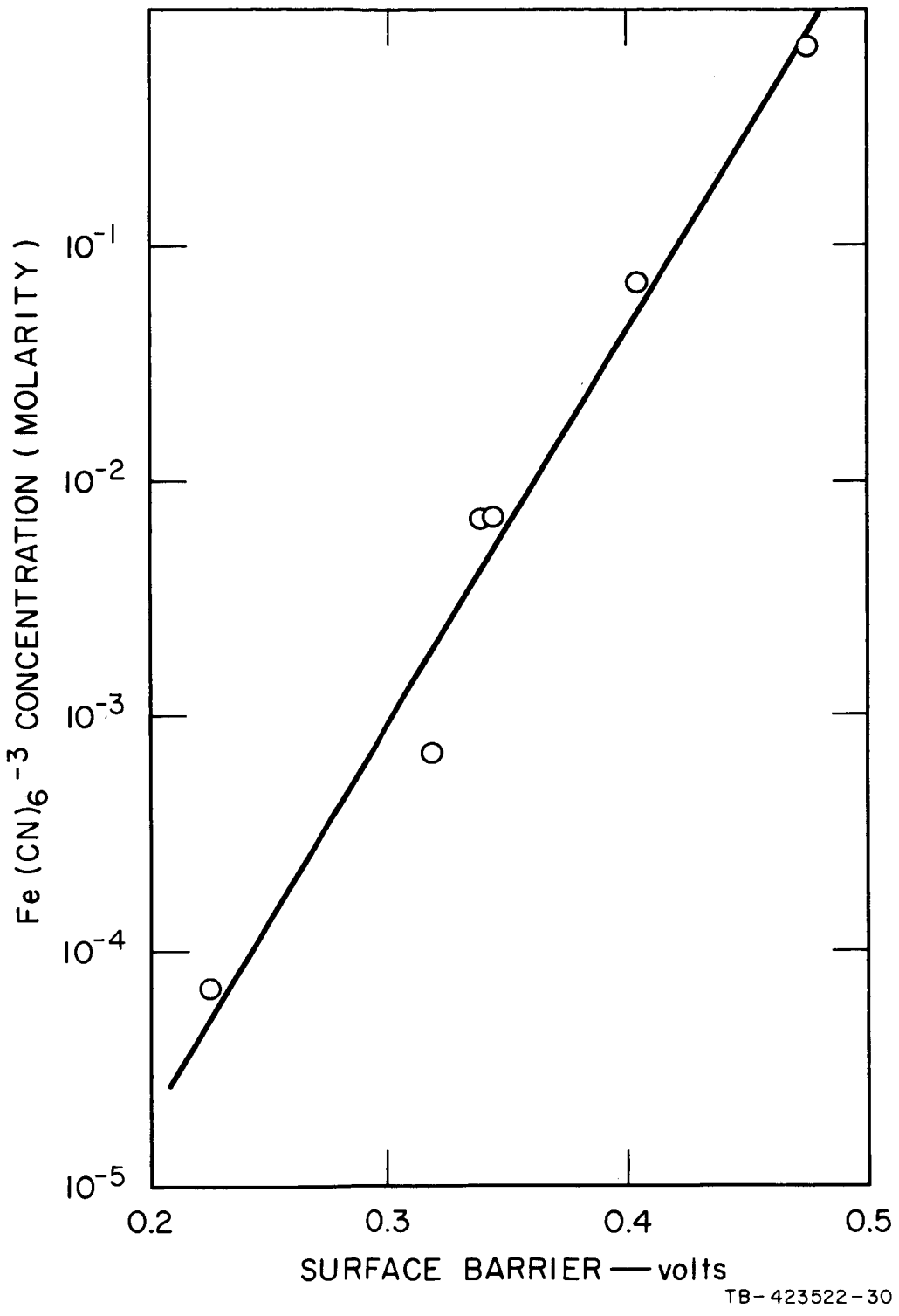
Fe (CN)6 -3 CONCENTRATION (MOLARITY)
10-1
10-2
10-3
10-4
10-5
0.2
0.3
0.4
0.5
SURFACE BARRIER — volts
TB-423522-30

FIG. 3

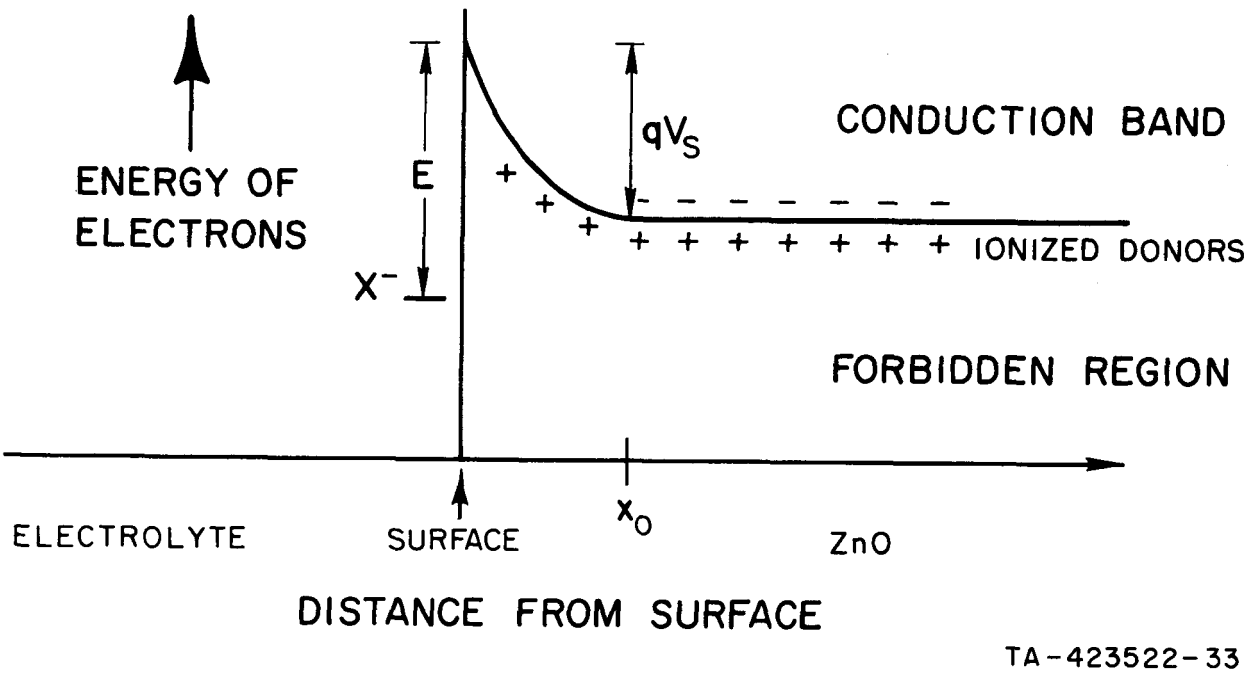
ENERGY OF ELECTRONS
E
X⁻
qVS
CONDUCTION BAND
IONIZED DONORS
FORBIDDEN REGION
ELECTROLYTE
SURFACE
xo
ZnO
DISTANCE FROM SURFACE
TA-423522-33

FIG. 4

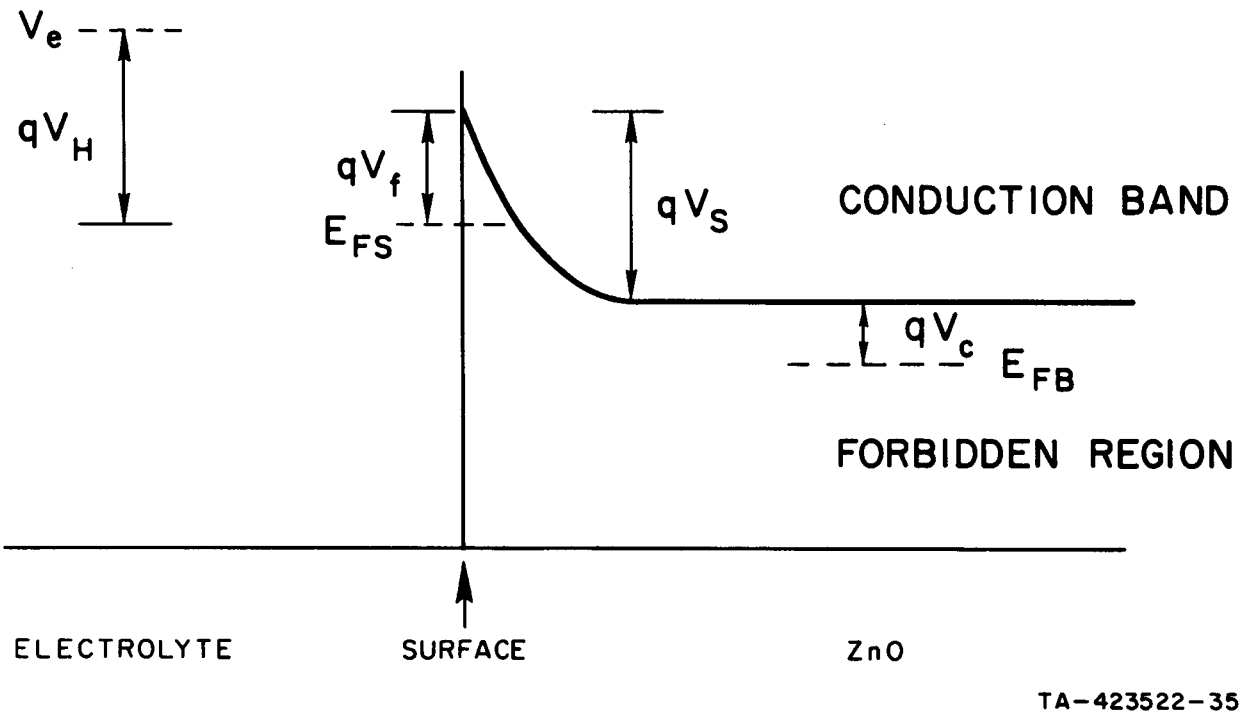
V_e
qV_H
qV_f
E_{FS}
qV_S
CONDUCTION BAND
qV_c
E_{FB}
FORBIDDEN REGION
ELECTROLYTE
SURFACE
ZnO
TA-423522-35

FIG. 5